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ABLATIVE PYROLYSIS OF MACROPARTICLES
OF BIOMASS

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ABLATIVE PYROLYSIS OF MACROPARTICLES OF BIOMASS

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ABSTRACT

Recent research has revealed that macroparticles of biomass can be pyrolyzed with a "solid convection" heat transfer technique to result in surface regression rates of over 3 cm/sec, which is $3\frac{1}{2}$ orders of magnitude faster than that attained with conventional gaseous and radiative heat transfer techniques. The extremely high heat fluxes attained by this technique pyrolyze the macroparticles of biomass without forming the usual layer of char (char usually insulates the substrate to force a slow pyrolysis reaction to occur with macroparticles). This observed laboratory phenomena is being used in the design of a unique 100 lb/hr research reactor to fast pyrolyze 1 cm wood chips in which the chips will be entrained into a reactor which utilizes centrifugally-enhanced, solid-convection heat transfer.

INTRODUCTION

In considering a chemical process, selecting a process which makes a high valued product rather than a mediocre valued product has an obvious economic advantage, if all other things are equal. That is why the conversion of biomass wastes to high octane gasoline rather than a boiler fuel was selected for further study at the Naval Weapons Center in the early 1970's. Conceptually, the process involved the very selective fast pyrolysis of the biomass to gases containing significant amounts of reactive hydrocarbons such as ethylene and propylene. These gases were compressed, purified, and then under heat and pressure the reactive hydrocarbons were reacted with themselves without catalysts to form low molecular weight polymers. The polymerization reaction is self-limiting such that about 90% of the polymers boil in the gasoline range. With polymer gasoline made in this manner, but from pure ethylene, the unleaded octane number was found to be in the low 90's. Polymer gasoline made from pyrolysis gases had the same distillation curve as that made from pure ethylene, indicating that the initial presence of acetylene, propylene, and butenes in the pyrolysis gases has little effect on the product. This allows the use of a very simplified gas purification system since the various C_2^+ hydrocarbons (larger than methane) do not need to be separated from each other. Gasoline yields of about 75 gallons per dry, ash-free ton of biomass were projected based on values obtained from the pyrolysis of municipal solid waste derived feedstock (ECO II by Combustion Equipment Associates) (1).

The process is relatively energy intensive such that the byproduct

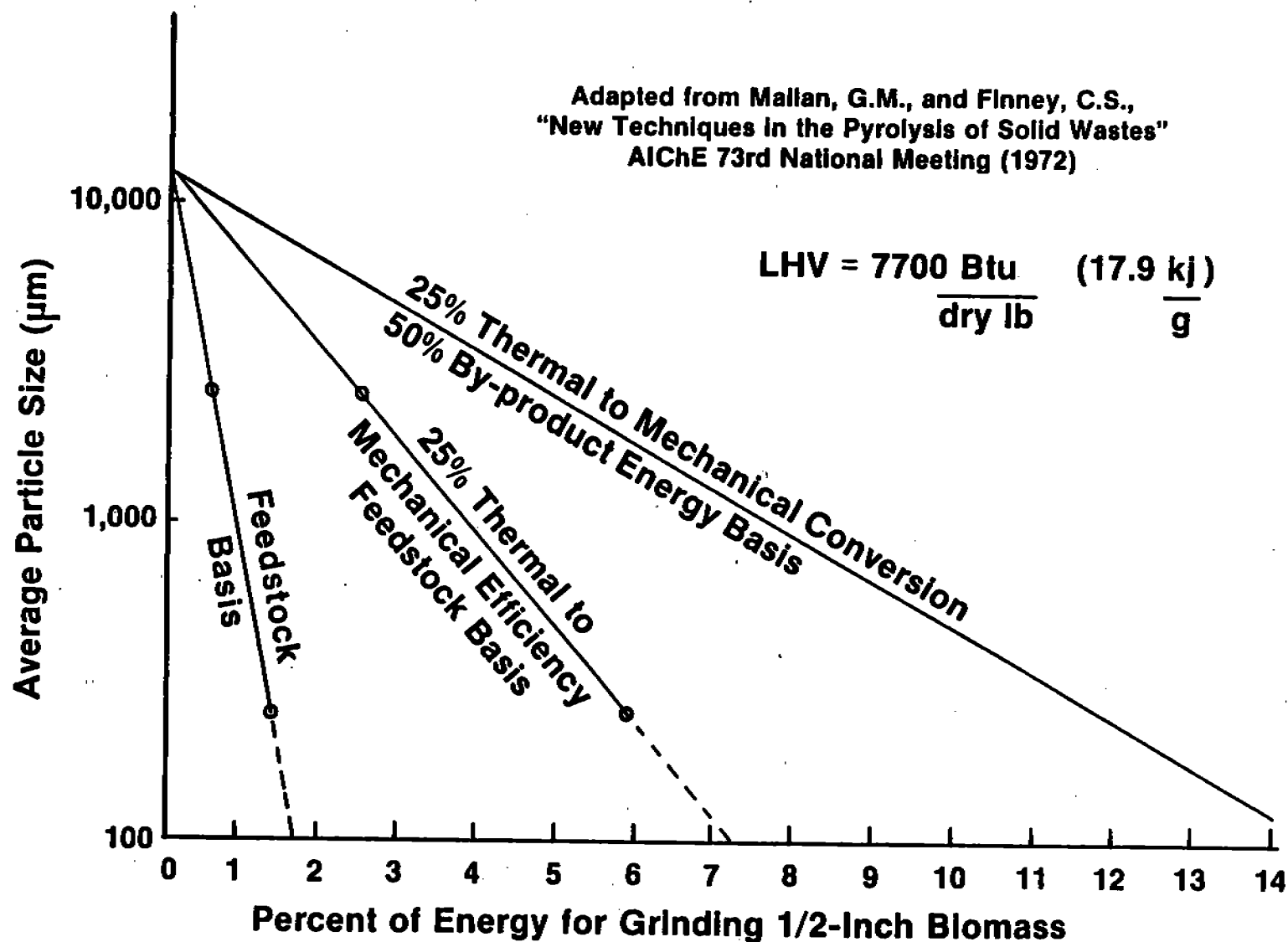
fuel gases, tars, and char (if any) would all be burned for process energy. The yields of the intermediate olefins were shown to increase with the amount of steam usage. This means that any improvement in the energy efficiency of the process, which can be converted to steam production, can be related to a small incremental increase in the potential yield of olefins. For example, a study of the energy required to recirculate carrier gases revealed that carbon dioxide required significantly more energy than the use of steam or the byproduct fuel gases. Furthermore, unless the capital expense of a larger hydrocarbon absorption tower, compressor, and a gas turbine (for energy recovery) were less than for a steam boiler, steam appeared to be a more energy efficient carrier than diluent gas. This conclusion is reinforced by the petrochemical industry's use of steam as the diluent gas when cracking naphtha to ethylene. Other means of increasing the system's efficiency would, of course, include the extensive use of heat exchangers to recover heat for steam generation. The low temperature waste heat, such as that formed by steam condensation at atmospheric pressure, would be used to heat air for feedstock drying (2).

In addition to these more obvious methods of increasing the energy efficiency of the process, the possible elimination of unnecessary, superfluous process steps was examined and found to have real potential. Figure 1 shows that the energy required for the conversion of 1 cm chips to 100 μ m powder is a small portion of the energy contained in the feedstock. However, in a typical industrial situation the energy put into the biomass for grinding is in the form of mechanical energy so that the true energy penalty for grinding is 3 to 4 times as high depending on thermal to mechanical conversion efficiencies. For 100 μ m particles, this amounts to $7\frac{1}{2}$ % of the energy contained in the feedstock or 10 to 15% of the energy available for process energy, which is quite significant. In addition, the hot ground feedstock would most likely be put into temporary storage where it would be allowed to cool and thereby lose all the energy put into it by the grinding step. Consequently, one of the valid criticisms of state-of-the-art fast pyrolysis is that a finely powdered feedstock is necessary to obtain the high heating rates for the particles to avoid the undesirable side reactions of pyrolysis such as char and water formation. A significant decrease in the process energy required could be attained if one could use 1 cm chips rather than 100 μ m powders for fast pyrolysis feedstocks.

The last effort with the China Lake entrained-bed pyrolysis reactor before the program was phased out at the Naval Weapons Center was the pyrolysis of pure cellulose, lignin, and birch flour. Due to mechanical difficulties with the system, only a preliminary screening of these feedstocks was obtained. The cellulose and the birch flour both produced about 12 to 14% by weight of the desired hydrocarbon product (C_7^+). This was considerably lower than had been attained with the ECO II material and is thought to represent suboptimal reaction conditions. The very significant results of this work concern the very small amount of char formed and its physical shape. From the cellulose pyrolysis, only 0.1% of the feedstock was converted

FIG. 1

Biomass Grinding Power Requirements



to char and part of that is thought to have been reactor scale. This result was predicted by the work done at MIT (3) in which a few milligrams of cellulose were sandwiched between electrically heated screens. However, the China Lake work demonstrated the phenomena in a continuous flow reactor with over 5 kilograms of cellulose involved in the reaction. This represents a scale-up of the phenomena by 4 or 5 orders of magnitude. The birch flour pyrolysis resulted in a $1\frac{1}{2}\%$ conversion to char which reflects the higher ash content of the wood flour. The calculated ash content for both the cellulose and the birch char is very similar at about 30%. This similarity in ash content may indicate that the very fine ash had a catalytic effect to cause condensation reactions to occur on its surface until the resultant tars decomposed to char to block the movement of reactants to the catalytically active sites. Examination of the birch-flour char confirmed that it was not typical of slow char forming reactions. Most of this char had no structure resembling the fibrous feedstock. Instead, the char had the appearance of being an agglomeration of $1\text{ }\mu\text{m}$ spheroidal particles as shown in Figures 2 through 4 (4,5). This type of char formation is contrary to the classical concept of pyrolysis and char formation, in which the virgin feedstock has a char layer through which heat must be conducted in counter flow to the off-gassing pyrolysis products. This concept of pyrolysis, although valid for slow pyrolysis, does not appear to be applicable to fast pyrolysis. One of the apparent anomalies noted in the ECO II pyrolysis work at China Lake was that the char had about the same bulk density as the ECO II feedstock (6). This was disturbing at the time because the slow pyrolysis concepts require that the feedstock particle be hollowed out by the process. This removal of 85% of the mass should have greatly reduced the bulk density even after allowing for some physical shrinkage of the outside dimensions. The char anomaly was not resolved until the birch flour char was examined microscopically and found not to be composed of skeletal remnants. The lack of char formation on the pyrolyzing surface of the biomass has a major impact on the ability to transfer heat into the particle.

The formation of char on the surface of slowly pyrolyzing biomass serves to act as a thermally insulating layer. Through this layer, the pyrolysis gases pass in counter-current flow relative to the heat needed for pyrolysis. This transpirational cooling of the char by the gaseous pyrolysis products (mostly steam formed by the slow dehydration reaction) greatly reduces the heat flux and consequently the pyrolysis rates. The rate of pyrolysis as measured by the equilibrium rate of advance of the char-wood interface is very slow and is about $3\frac{1}{2}$ cm per hour with radiative and free convective exposure to temperatures of 500 to 1000°C (ASTM-E119) (7). In contrast to this slow rate, the pyrolysis of $250\text{ }\mu\text{m}$ particles in an estimated 50 ms residence time in the China Lake entrained flow reactor suggests a fast pyrolysis rate in excess of 900 cm per hour or 0.25 cm per second. Although this estimated rate is very high, the maximum rate of pyrolysis probably was not attained due to the intermittent contact of the turbulently entrained particle with the hot tube wall.

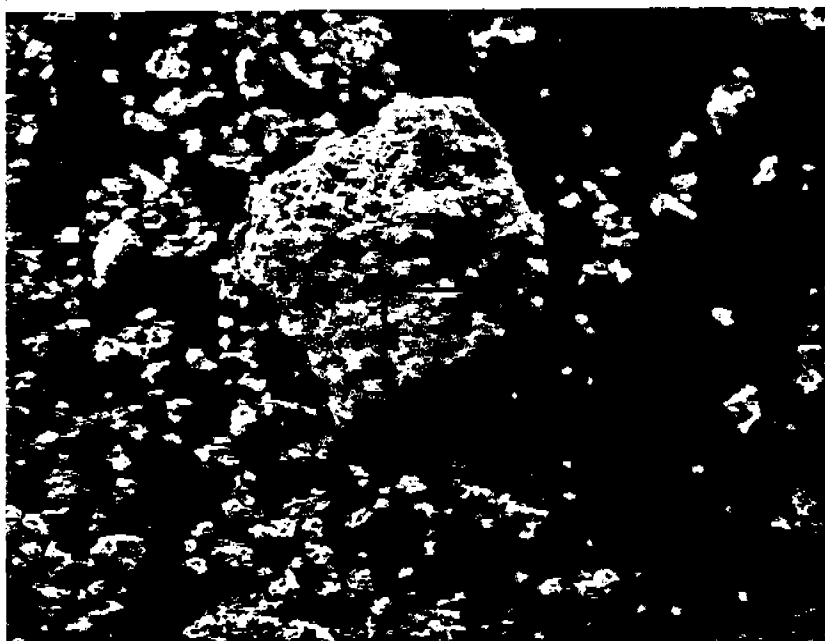


Fig. 2 SEM Photograph
of Birch Char (147X)

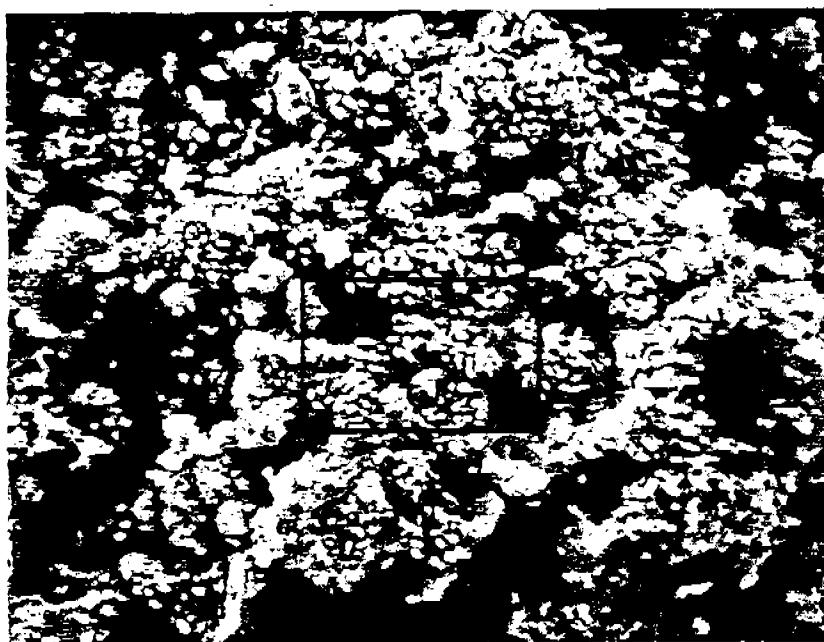
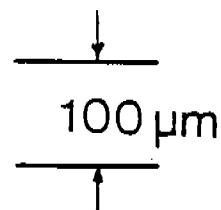
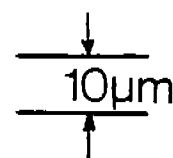


Fig. 3 SEM Photograph
of Birch Char (853X)



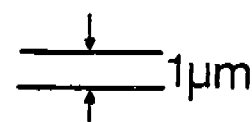
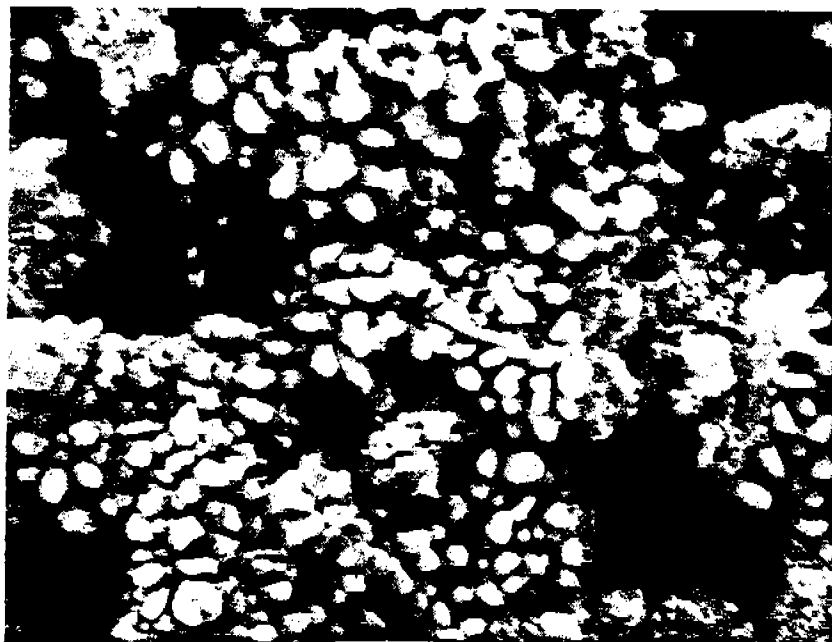


Fig. 4 SEM Photograph of Birch Char (2500X)

The importance of physical contact of the pyrolyzing biomass particle with the hot wall is readily apparent with the proper assumptions. If it is assumed that the wall temperature is 1800°F ($\sim 1000^{\circ}\text{C}$), that the surface of the pyrolyzing biomass is at 600°F (315°C), and the absorptivity is a generous 0.85, then the radiative heat flux to the particle is about 35,000 BTU/hrft² ($\sim 12 \text{ w/cm}^2$). One concept of pyrolysis is that the biomass decomposes first to pyrolytic oils. With the same relative temperatures, conducting heat through a thin 10 μm layer of this pyrolytic oil having an assumed conductivity of 0.08 BTU ft/ft²hr°F results in a phenomenal heat flux of nearly $3 \cdot 10^6$ BTU/hrft² (1000 w/cm^2). Whether or not this high heat flux to the virgin substrate could be attained in reality depends upon how well the assumed conditions can be met. The reactor wall temperature would be very difficult to maintain in a steady state since petrochemical cracking furnaces typically have heat fluxes of only 10,000 to 50,000 BTU/hrft² (3 to 15 w/cm^2) even in the radiative sections. Without resorting to focused light energy sources (e.g., laser or solar power tower), high heat fluxes to the wall could be supplied by condensing sodium vapors as in a heat pipe. At these fluxes the temperature drop through a 0.1 inch (0.25 cm) stainless steel wall is on the order of several hundred degrees. However, if the pyrolyzing particle were to be in a dilute entrained flow and in relative motion to the hot reactor wall, the heat flux to the particle could be much higher than the average heat flux through the wall. This "forced solid convective" heat transfer would allow the wall to recover its initial temperature between the passage of each particle. The particle must be kept in firm contact with the wall to maintain the high conductive heat flux. Maintaining the liquid pyrolytic oil film at a minimum thickness requires that the particle be forced to the wall to extrude the oil out. Relative motion between the wall and the particle will also aid in wiping off the oil (and any char) as it is formed. The required conditions for fast pyrolysis of macroparticles appeared to fit an externally heated cyclone reactor as will be discussed, but the demonstration of the concept was needed before committing the necessary resources to build a unique reactor design.

ABLATIVE HOT-WIRE PYROLYSIS

The demonstration of the physical rate at which pyrolysis proceeds is very difficult in an entrained flow reactor. However, a few conceptual changes to the discussion above allows for a very easily constructed qualitative experimental apparatus. If the biomass macroparticle is held stationary while the hot stainless steel surface slides past, the physical rate of pyrolysis could be measured. Since the biomass is rapidly offgassing, air will have a very difficult time to diffuse into the pyrolysis site. If the quantity of pyrolysis products formed is kept small, they will cool before they have mixed with sufficient air to ignite.

To demonstrate the fast pyrolysis of macroparticles (e.g., tongue depressors) a hacksaw frame was fitted with a 0.010 inch (254 μm) diameter nichrome wire. The wire was electrically insulated from the frame and attached to a transformer to provide about 20 volts. With

this simple arrangement, one can "saw" through biomass as though it were a thermoplastic like polyethylene or polystyrene. The sawing action produces smoke which normally does not ignite. The width of the cut is slightly less than the width of the cutting wire. If the "sawing" action is started without the wire being hot, only a negligible cut can be made. Turning on the electricity to the wire results in the saw suddenly having a lubricated feeling as the biomass pyrolyzes to form the oils and vapors. It is not definitely known at this time if the biomass forms only liquids which then vaporize or if some gases are formed concurrently with the liquid. However, the formation of gases between the biomass and the hot steel surface would drastically reduce the heat transfer rates. Microscopic examination of the best "cut" (pyrolyzed) surfaces reveal no char present and that the cell structure can be clearly seen through a light-colored tar layer which appears as a coat of varnish. The hypothesis that wood pyrolyzes first to tar with very little concurrent gas formation is supported by the lack of a foamed appearance on the "cut" surface. Thin pieces of biomass cut fastest with the least evidence of char formation due to the wire cooling too much with the thicker sections. The red hot wire is visibly cooled and darkened as it passes through even thin biomass such as paper or wood veneers.

A more sophisticated experimental apparatus was constructed to obtain quantitative data for the hot-wire-fast-pyrolysis phenomena. A small DC motor was obtained and fitted with a double spool so that while the nichrome wire was winding off one side of the spool, the other side could be winding it back up. The wire passes over an electrically conductive graphite pulley to the pyrolysis zone and then to another graphite pulley. A microswitch was placed so that the deflection of the hot wire could signal the start and end of the cut. This elapsed time divided by the width of the biomass gives the physical rate of pyrolysis. The wire also passes around an odometer wheel which trips a microswitch for every revolution. By counting the blips on a recorder, wire speed is ascertained. The pressure at the wire-biomass interface is calculated from the biomass weight, the thickness of the biomass and the wire. Measurement of the temperature of the wire as it enters and exits the biomass would provide indications of heat of reaction, heat transfer rates, and pyrolysis temperatures. It appears that optical pyrometry is the most promising approach to the wire temperature measurements. Automatic commercial optical pyrometers unfortunately are made to look at larger "targets" than the thin wire. Manually operated "disappearing filament" optical pyrometers are impossible to operate accurately in the second or so available to take the measurement. The little known technique of using infrared sensitive film to record temperatures appears to be very promising for the hot wire system, but technical difficulties and priorities have thus far precluded obtaining quantitative wire temperature data. However, with wire temperatures estimated to be at 1500 to 1800°F (800 to 1000°C), hand-held hardwood tongue depressors have been cut at rates of 1 cm/sec and 3 cm/sec at wire speeds of 10 and 20 cm/sec respectively. With thin birch veneer, cutting rates of 3 1/2 cm/sec were attained with wire speeds of about 10 cm/sec. Preliminary transient heat transfer calculations suggest the biomass is heated

only to a depth of about 20 μm , which implies a heating rate of about $5 \cdot 10^5$ $^{\circ}\text{C}/\text{sec}$.

Other means of attaining ablative pyrolysis which were demonstrated included a "friction saw" made of a smooth disk of stainless steel fitted to a hand-held rotary saw. A relief was machined into the disk to minimize the rubbing contact of the sides of the disk on the walls of the cut. The friction of the circumference of the disk against the wood caused it to locally heat enough to cause pyrolysis. The charless cutting front passed through the wood fast enough to avoid charring the wall of the cut. The resulting cut surface was very smooth and had a polished appearance. The use of a friction saw to cut aluminum and stainless steel has been known for quite some time, but its usefulness to cutting wood is a newly recognized phenomena.

A hand-held tesla coil used for checking out electronics was also used to demonstrate fast pyrolysis. With very short duration discharges through a wooden tongue depressor, very small, crooked, charless holes were formed initially. Longer duration discharges resulted in larger diameter holes which had charred walls and through which light could pass.

Although much more data need to be generated with the hot wire apparatus, the tentative conclusions are that: biomass can indeed be pyrolyzed without the formation of an insulative char layer and that pyrolysis rates, which are $3 \frac{1}{2}$ orders of magnitude greater than slow pyrolysis rates, can be achieved with the proper combination of steel surface temperatures, relative motion, and pressure. Due to all of the implications that fast pyrolysis of macroparticles was indeed demonstrated in the laboratory, an engineering demonstration of the concept was given top priority.

ENGINEERING DEMONSTRATION OF ABLATIVE FAST PYROLYSIS OF MACROPARTICLES

Initial concepts for the engineering demonstration of the macroparticle pyrolysis involved the use of 1 cm wood chips entrained by a supersonic steam flow into a toroidally shaped reactor. The chips would be centrifuged to the outside wall of the toroid where they would be pyrolyzed. However, it was soon realized that this design would use only a small portion of the toroidal surface for heat transfer, i.e., the major diameter of the toroid. Subsequently, the tangential entry for the feedstock was changed from a simple angle to a compound angle which would cause the particles to travel a helical path as they traveled around the inside of the toroid. The particles would then extract heat from the entire inside surface of the toroid. The relative diameters of the toroid under consideration were such that the particle was being subjected to extremely high "g" forces due to the helical motion in the toroidal tube and relatively low "g" forces due to the toroid itself. After comparing ease of construction, it was decided to straighten out the toroid to form a simple cyclone reactor.

The cyclone reactor design is conceptually very simple, as shown in

Figure 5. The biomass, as large as 1 cm particles, are accurately metered to the steam ejector with a gravimetric weigh feeder. This screw feeder is on an electronic scale which constantly adjusts a volumetric feeder to deliver a desired mass rate of a nominal 100 lbs/hr (45 kg/hr). A twin screw in the feeder will be used with finely powdered feedstock, whereas a 45 mm single screw will be used with wood chips. The steam ejector uses 100 lbs/hr of superheated steam at 200 psig (1450 kPa) and 1400°F (760°C). The steam serves to entrain the particles into the 6 inch (15 cm) diameter by 28 inch (71 cm) cyclone reactor at speeds up to 375 ft/sec (114 m/s), as well as to dilute the gases and thereby reduce the partial pressure of the pyrolysis products. If 1 cm cubes of biomass were to be fed at 100 lbs/hr (45.4 kg/hr) there would be 30 particles per second spaced an average of 10 ft (3 m) apart in the steam ejector stream. In the cyclone reactor, the biomass particles initially experience 19,000 "g's" to force them to the red hot wall, as shown in Figure 6. This produces a force of about 30 lbs (140 N) under a 1 cm cube of biomass or about 140 psia (1000 kPa) between the wall and the cube. If the tar is wiped off the biomass as fast as it is formed, the tar will be under the fast moving 1 cm chip for only 0.1 ms. Three electric heater systems are to provide the energy needed for pyrolysis. These heater systems will be independently controlled and the energy consumption independently monitored. Although the solid biomass particles are trapped in the cyclone reactor for an estimated 300 ms until the 1 cm particle is vaporized, the gases and vapors are free to leave through the exit located on the center line of the cyclone. The average gaseous residence time in the cyclone is estimated to be between 75 and 175 ms. A purged three inch (7 1/2 cm) diameter quartz sight glass will be located near the tangential entry so that the pyrolyzing particles may be photographed with SERI's 10,000 frame per second movie camera.

Downstream of the cyclone reactor is a 2 inch (5 cm) diameter vapor cracker reactor which is 17 feet (5 m) long. The gases and vapors will have an additional 70 to 150 ms residence time in the vapor cracker. The vapor cracker will be electrically heated by six independently controlled and monitored heaters. Due to the inability of large solids to escape the cyclone reactor, all tar vapors will have a chance to be cracked, whereas in a purely entrained-flow situation the larger particles are still producing tar vapors at or near the exit of the system.

Gas samples may be withdrawn from three locations in the cyclone pyrolysis reactor and six locations in the vapor cracker. This reactor system will be able to generate data related to the energy requirements at the various stages of pyrolysis as well as determining the intermediate product distribution of the gases at various residence times and temperature histories (cracking severities). The independently controlled heater sections will allow a variety of temperature profiles to be forced onto the cyclone reactor and the vapor cracker. The capabilities of this reactor system are very similar to that used by the Europeans to study hydrocarbon cracking to produce olefins (9). The use of Incoloy 800H for the cyclone reactor

FIG. 5

Ablative Macroparticle Pyrolysis Flow Schematic

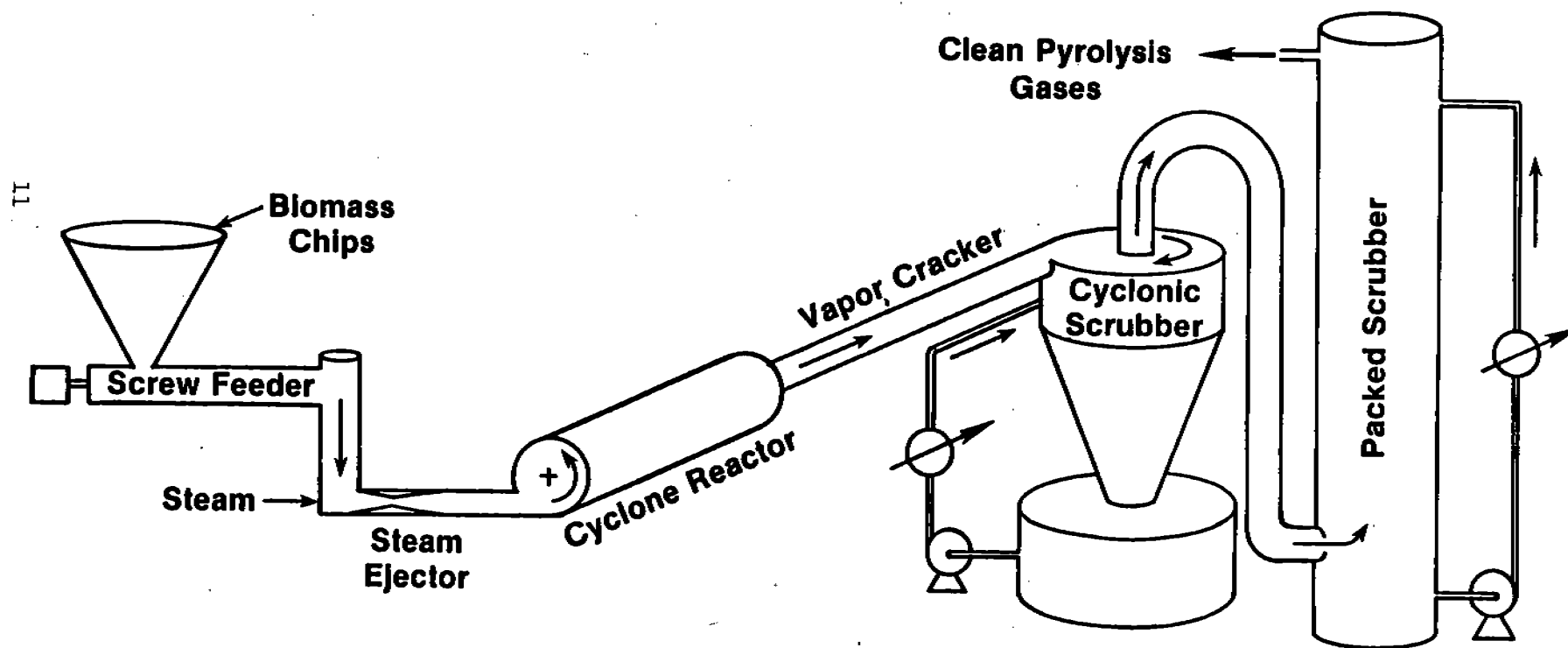
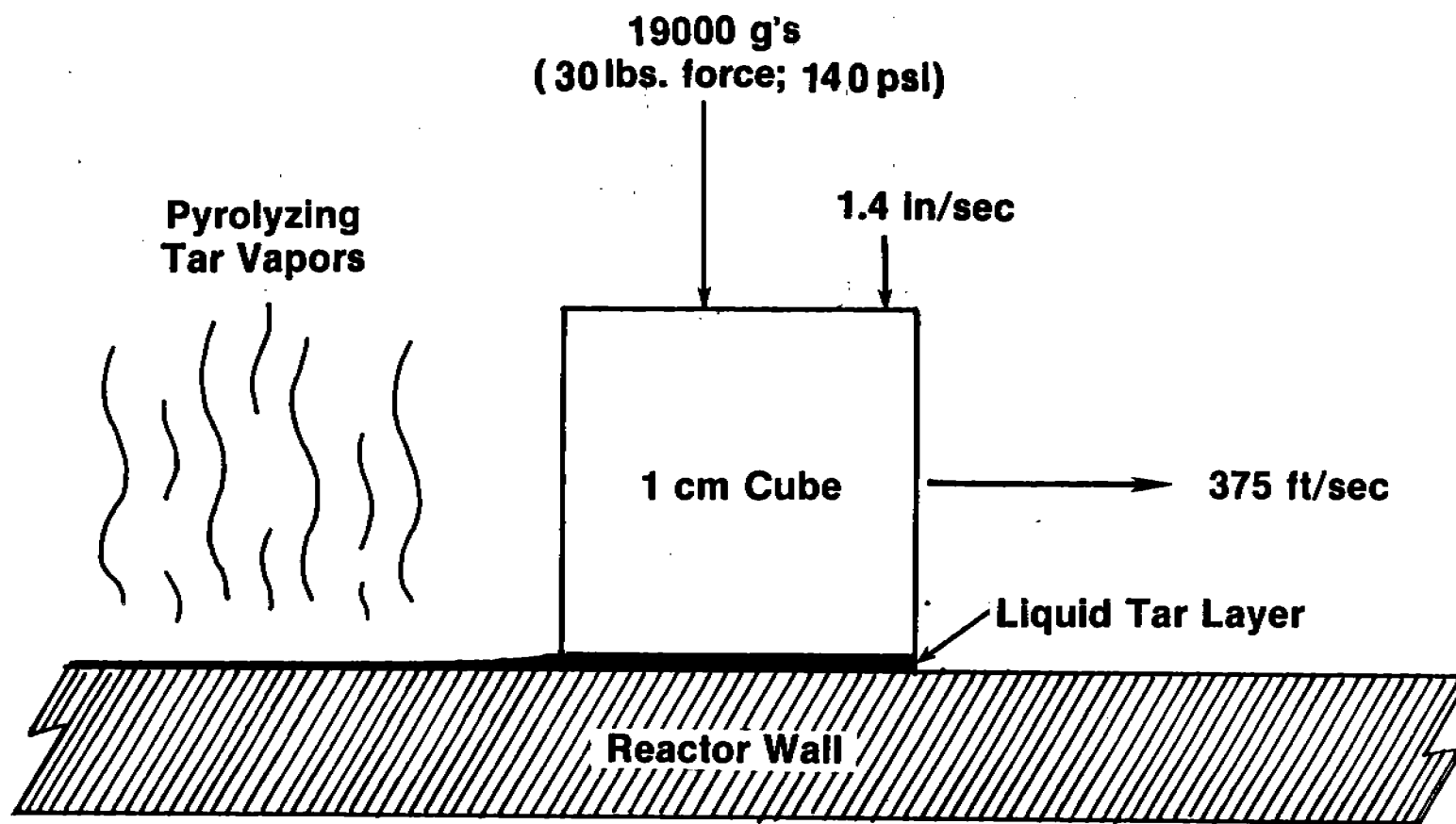


FIG. 6

Macroparticle Pyrolysis Concept



and the vapor cracker reflects naphtha cracking state-of-the-art (10). The use of the gravimetric weight feeder system will allow the instantaneous comparison of biomass flow into the reactor to gas flow out of the system and provide several data points per experimental run. The capabilities of this new reactor system are relatively sophisticated compared to previous reactors.

Downstream of the vapor cracker, the pyrolysis stream will be quenched and cooled to slightly below the steam dew point in a cyclonic scrubber using high pressure water sprays. The small amount of anticipated char, tar, and ash will accumulate primarily in this cyclonic spray system. A small amount of char-tar-ash slurry will be constantly slipstreamed to the flare for incineration. The cooled gaseous stream will then go to an irrigated packed scrubber where steam will condense and help to coalesce the anticipated entrained tar mists. The cooled, clean gases will then pass to an orifice meter before being flared off. The entire pyrolysis reactor system will be operated at only slightly above atmospheric pressure to maximize the olefin formation in the gases. Conversion of these gases into gasoline, alcohols, or petrochemical feedstocks will be addressed in future programs.

The major components for this 100 lb/hr macroparticle engineering demonstration have been ordered with deliveries to begin in mid-October 1980. The equipment will be assembled next to SERI's oxygen gasifier unit with a probable completion date of late December 1980. Shakedown and experimentation will commence in January 1981.

CONCLUSIONS

New insights into biomass fast pyrolysis have revealed that char formation can be a secondary rather than a primary reaction, so that virtually no char is formed with the proper heat flux and primary tar removal. This hypothesis was shown to be valid when using a red-hot wire drawn across macroparticles of biomass such as wood veneer and tongue depressors. Pyrolysis rates $3\frac{1}{2}$ orders of magnitude greater than slow pyrolysis were demonstrated. Because the heating is localized, only the pyrolyzing surface is heated so that the size of the particles is of very little importance. Additional data will be generated with the hot wire apparatus to look at wire temperature, speed, and pressure relationships.

A practical 100 lb/hr (45 kg/hr) reactor to utilize these insights into fast pyrolysis has been designed and is being procured. This engineering demonstration reactor will be able to pyrolyze particles up to 1 cm in diameter and is the smallest size reactor practical for these large particles. The system will be operating during FY81 to demonstrate the ablative fast pyrolysis of biomass macroparticles to produce gases rich in olefins for gasoline, alcohol, or petrochemical production.

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